PATENT ABSTRACTS OF JAPAN

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(54) PIEZOELECTRIC MATERIAL COMPOSITION OF ALKALI METAL- CONTAINING NIOBIUM OXIDE

(57)Abstract:

PROBLEM TO BE SOLVED: To provide an alkali metal-containing niobium oxide piezoelectric material that has the sintering properties that can give sintered products through the known sintering method under normal pressure, the temporal stability and temperature stability.

SOLUTION: A compound including Cu is added to a solid solution that is constituted with the formula: $K_{1-x}Na_xNbO_3$ (x =0-0.8) so that the amount of Cu element may be 0.001-5 mol.% to produce a high piezoelectric material with good sintering behavior and high piezoelectric properties. In another case, the addition of 10 mol.% of Li and 20 mol.% of Ta to a solid solution that is represented by the formula: $Li_x(K_{1-y}Na_y)_{1-x}(Nb_{1-z}Ta_z)O_3$ (x=0.001-0.2, y=0-0.8, z=0-0.4) gives a material having high temperature properties. These piezoelectric materials can be prepared by conventional sintering process under normal pressure.
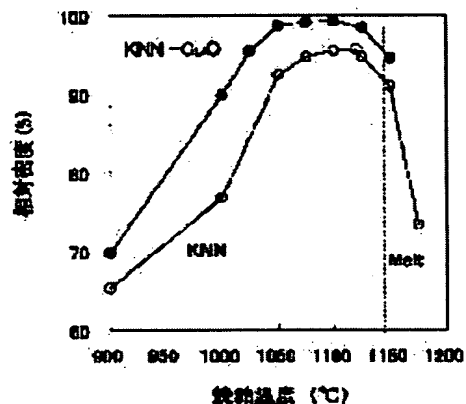
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* NOTICES *

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CLAIMS

[Claim(s)]
[Claim 1] The alkali-metal content niobic-acid ghost system piezoelectric-material constituent which adds and/or dissolves one sort or two sorts or more of matter chosen from Cu, Li, and Ta as the solid solution expressed with an empirical formula (ANbO3) (A : alkali metal), and is characterized by the bird clapper.
[Claim 2] The alkali-metal content niobic-acid ghost system piezoelectric-material constituent according to claim 1 by which the aforementioned empirical formula is expressed with K1-xNaxNbO3 (however, x=0-0.8).
[Claim 3] The alkali-metal content niobic-acid ghost system piezoelectric-material constituent according to claim 1 by which the aforementioned empirical formula is expressed with Lix (K1-yNay) 1-x (Nb1-zTaz)O3 (however, x= 0.001 to 0.2, y= 0 to 0.8, z=0-0.4).
[Claim 4] One sort or the two aforementioned sorts or more of matter is the compounds containing Cu element, and Cu is 0.001-5 mol % addition and/or the alkali-metal content niobic-acid ghost system piezoelectric-material constituent according to claim 2 which dissolves and is characterized by the bird clapper in the amount of elements.
[Claim 5] one sort or the two aforementioned sorts or more of compounds -- the amount of each elements -- 0-5-mol % -- the alkali-metal content niobic-acid ghost system piezoelectric-material constituent according to claim 3 characterized by adding

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] this invention relates to the alkali-metal content niobic-acid ghost system piezoelectric-material constituent used for the knocking sensor of the engine for automobiles etc. in more detail about a niobic-acid system piezoelectric-material constituent.
[0002]
[Description of the Prior Art] Conventionally, piezoelectric material is used for the knocking sensor of the engine for automobiles. Piezoelectric material will be divided into what roughly classifies and contains the lead system matter, and the thing which does not contain the lead system matter, and these will be chosen and used according to the use. By the way, like known, lead is a toxic substance, the piezoelectric material containing this lead system matter will also contain a toxic substance, and the handling and use will take consideration to it. Then, a piezoelectric material equipped with a high property will be required, without containing toxic substances, such as lead system matter.
[0003] for example, densification of the material is carried out to the piezoelectric material which does not contain the aforementioned lead system matter by raising the degree of sintering of material by adding various kinds of accessory constituents into the material of a niobic-acid (NbO_3) system -- making -- passing -- the time -- stability -- it is going to raise -- the thing is known Thus, if a degree of sintering increases, the component and phase of material can precise-turn and can carry out densification. Therefore, an electromechanical coupling coefficient and a mechanical quality factor are obtained comparatively highly. Moreover, since a toxic substance is not included, safety is high, and piezoelectric material with high piezo-electric property and stability will be obtained.
[0004] Various things are used for the accessory constituent added into the material of such a niobic-acid system. For example, what adds manganese oxide to the constituent which consists of empirical-formula $KNbO_3$-$NaNbO_3$-$LiNbO(s)_3$ is indicated by JP,50-47193,A, and what adds an aluminum oxide 0.02 to 2.0% of the weight, and adds an iron oxide in 0.001 - 0.019% of the weight of the range to the constituent constituted from general formula $Na_{1-x}Li_xNbO_3$ ($0.02<=x<=0.30$) by JP,60-52098,B is indicated. By promoting the degree of sintering of material, densification of the relative density is carried out, a mechanical strength raises an electromechanical coupling coefficient by this, and these [both] obtain a large material.
[0005]
[Problem(s) to be Solved by the Invention] However, although the piezoelectric material of the aforementioned niobic-acid system has the outstanding property, it is inferior to stability, such as the degree of sintering of material, temperature stability to an elevated temperature, and stability with the passage of time that shows the fall of the material property accompanying lapsed days. therefore, material -- more than a recrystallizing temperature -- fabricating -- and -- pressurizing (hot pressing) -- it is had and produced Hot pressing has the problem that a sintered compact with it cannot be manufactured, although a high-density sintered compact is obtained at low temperature compared with the so-called ordinary-pressure sintering process which fabricates material by the pressure and usually

sinters it. [a high and manufacturing cost and] [big] Therefore, although densification of the material produced with hot pressing was carried out by the operation of pressurization, about temperature stability or stability with the passage of time, it was not enough and had the problem that production cost was high.

[0006] Then, in the niobic-acid system piezoelectric material which does not contain lead system material, the technical problem which is going to solve this invention is in the production method to have by the existing ordinary-pressure sintering process, and offer a producible niobic-acid system piezoelectric-material constituent while finding out a substitution dissolution-ized agent and/or an additive that the temperature characteristic and stability with the passage of time should be raised.

[0007]

[Means for Solving the Problem] one sort or two sorts or more of matter with which the niobic-acid system piezoelectric-material constituent according to claim 1 applied to this invention in order to solve this technical problem was chosen as the solid solution expressed with an empirical formula (ANbO3) (A : alkali metal) from Cu, Li, and Ta -- addition -- and -- or it dissolves and let a bird clapper be a summary

[0008] In this case, as an alkali metal, a thing [adopting K and Na, adding or making these dissolve like] according to claim 2 is desirable. In this case, the aforementioned solid solution is expressed with empirical-formula K1-xNaxNbO3 (however, x=0-0.8).

[0009] Moreover, it is desirable to adopt K and Na, it to be desirable to add or to make these dissolve, to adopt Li and Ta as the aforementioned matter by which selection is carried out, and to make these add or dissolve as an alkali metal like invention according to claim 3 in a case according to claim 1. In this case, the aforementioned solid solution is expressed with an empirical formula Lix (K1-yNay) 1-x (Nb1-zTaz)O3 (however, x= 0.001 to 0.2, y= 0 to 0.8, z=0-0.4). Since liquid phase sintering of it is carried out in case Li sinters, it acts as a sintering acid, and Ta also stabilizes dielectric loss while it acts on the domain in the solid solution and stabilizes a domain. Piezoelectric material with a sufficient property can be offered by these operations. And the addition of Li in this case had the problem of reducing a piezo-electric property less than [0.1 mol %] or more than 20 mol %. Therefore, the optimal amount is 0.1-20-mol %.

[0010] Moreover, the compound containing Cu element may be adopted, in a case according to claim 2, this may be added so that Cu may become 0.001-5-mol % in the amount of elements, and/or you may make it dissolve like invention according to claim 4 to it as the aforementioned matter by which selection is carried out. Since the compound containing Cu element acts as a sintering acid of the solid solution and improvement in relative density can be aimed at by this, material with a sufficient property is obtained. Furthermore, since it has the effect which the compound containing Cu element acts on the domain in the solid solution, and stabilizes a domain, improvement in stability with the passage of time can be aimed at, and piezoelectric material with a property sufficient also about this can be offered. However, if the addition of the compound containing Cu element added in this case is less than [0.001 mol %], it will not act as a sintering acid, and when it is more than 5.0 mol %, there is a problem that a property falls. Therefore, the optimal amount is 0.001-5.0-mol %.

[0011] furthermore -- as another operation gestalt in a case according to claim 3 -- being according to claim 5 -- like -- one sort or the two aforementioned sorts or more of compounds -- each and the amount of elements -- 0-5-mol % -- you may add

[0012]

[Embodiments of the Invention] Hereafter, the example of this invention is explained in detail with reference to a drawing. The manufacturing process of the sample in this invention is explained first. In addition, either ordinary-pressure sintering or pressure sintering is OK as the sintering process used for manufacture, and all the heating methods, such as electric furnace heating, microwave heating, high-frequency induction heating, and infrared heating, are possible for it also about the heating method. Moreover, you may carry out by whichever within an oxygen flow and in air also about the state at the time of sintering. Then, in this example, it considered as the inside of an oxygen flow (5% - 100% of oxygen) using the existing ordinary-pressure sintering process used when manufacturing ceramic

material. A property is explained from the example and the measurement result of the manufactured sample below.

[0013] (Example 1) CuO was added in the basis sample which consists of empirical-formula K1-xNaxNbO(s)3 (0<=x<=0.8), and this invention sample (the first sample : KNN-CuO) was manufactured. Raw material blended each powder of K2CO3 of 99% or more of purity, and NaHCO3 and Nb 2O5 so that it might become the empirical formula of K0.5Na0.5NbO3, and it obtained a total of a 50g weighing capacity object. And it mixed with the ball mill for 20 hours using the acetone, after drying this end of mixed powder, temporary quenching was performed at 900 degrees C for 5 hours, and the powder which cracks this, carries out a particle size regulation with a #60 mesh sieve, and has the crystal phase of K0.5Na0.5NbO3 was created.

[0014] Next, 0.01-mol CuO was added to one mol of crystal powder of aforementioned K0.5Na0.5NbO3, and it had with the ball mill again using the acetone, and mixed and ground for 20 hours, and this was ground to the powder of 0.3-0.4 microns of mean particle diameters with the #60 mesh sieve. A polyvinyl butyral is added to this ground powder 2% of the weight, it was dried, the particle size regulation was carried out with the #60 mesh sieve, it had with 1 shaft press of 2 ton/cm2, and the press object with a diameter [of 18mm] and a thickness of about 2mm was produced.

[0015] And in the flow of oxygen 0.3 L/min, by 5 degrees C of programming rates, and min, it was made to go up to 600 degrees C, and held for 1 hour, and the aforementioned press object was heated to 1050 degrees C with the aforementioned programming rate and this speed, and was held for further 1 hour. And it cooled to the room temperature (about 25 degrees C) by 5 degrees C/min, and the sintered compact was produced this time. Next, grinding and after grinding and processing it, it had Au electrode by the spatter and the vertical side of a disk-like sample was coated with it, the vacuum evaporationo of this sintered compact was carried out to the thickness of 1mm, and the diameter of 15mm, in the 100-degree C silicone oil, the seal of approval of the 3kV [/mm] electric field was carried out for 10 minutes, polarization processing was carried out, and it gave piezoelectric. In this way, after leaving the done sample for 1 hour, the various properties were measured.

[0016] In this way, the measurement result in the stage which passed after polarization of the first manufactured sample (KNN-CuO) for 1 hour is shown in Table 1, and the measurement result in the stage which passed after polarization of this sample on the 28th is respectively shown in Table 2. Moreover, in order to perform comparison contrast of these measurement results, the measurement result of the basis sample (KNN) sintered at 1100 degrees C which has not added CuO is also doubled and shown.

[0017]

[Table 1]

KNN－CuOの測定結果（分極後1時間）

	本発明品（第一試料）	比較品（基試料）	
試料名	KNN－CuO	KNN	
組成式	$K_{0.5}Na_{0.5}NbO_3$ $+0.01$モルCuO	$K_{0.5}Na_{0.5}NbO_3$	
測定項目			
相対密度（％）	98.8	96.2	★
圧電特性			
電気機械結合係数（kp）	0.389	0.334	★
圧電定数（d31 pm/V）	29.2	37.6	
圧電定数（d33 pm/V）	96.2	115	
圧電定数（g31 10^{-3}Vm/N）	13.92	9.90	★
圧電定数（g33 10^{-3}Vm/N）	46.1	30.3	★
弾性特性			
機械的品質係数（Qm）	1408.2	100.6	★
誘電特性			
誘電率（E33t）	237	429	
誘電損失（tanδ）	0.0045	0.0356	★
相転移温度			
キュリー温度（℃）	415	415	
温度変化率			
誘電率（％/-50～100℃）	27	93	★
抵抗率（Ω・cm）	1.32E+13	7.67E+10	★

（注）★：CuOにより向上している特性

[0018]
[Table 2]

KNN－CuOの測定結果（分極後２８日）

	本発明品（第一試料）	比較品（基試料）	
試料名	KNN－CuO	KNN	
組成式	$K_{0.5}Na_{0.5}NbO_3$ +0.005モルCuO	$K_{0.5}Na_{0.5}NbO_3$	
測定項目			
相対密度（％）	98.8	96.2	★
圧電特性			
電気機械結合係数（kp）	0.377	0.329	★
圧電定数（d31 pm/V）	27.8	38.6	
圧電定数（d33 pm/V）	96.7	115	
圧電定数（g31 10^{-3} Vm/N）	13.59	9.30	★
圧電定数（g33 10^{-3} Vm/N）	46.1	30.3	★
弾性特性			
機械的品質係数（Qm）	1661.9	85.6	★
誘電特性			
誘電率（E33t）	231	470	
誘電損失（tanδ）	0.0045	0.0890	★
相転移温度			
キュリー温度（℃）	415	415	
温度変化率			
誘電率（％/-50～100℃）	27	93	★
抵抗率（Ω・cm）	1.32E+13	7.67E+10	★

(注) ★：CuOにより向上している特性

[0019] As a parameter, an electromechanical-coupling-coefficient [in the direction vibration of a path besides relative density (%)] (kp), mechanical quality-factor (Qm), and voltage-output piezo-electricity coefficient (g31, g33), a charge output piezo-electricity coefficient (d31, d33), a dielectric constant (epsilon33 T/epsilon 0 (value in 1kHZ)), dielectric loss (tandelta (value in 1kHZ)), etc. were mentioned.
[0020] In addition, the resonance antiresonating method of JEOL material Semiconductor Equipment & Materials International standard EMAS-6007 was used for measurement and evaluation of this sample. In addition, the Curie temperature (Curie point) which shows the phase transition temperature from a ferroelectric phase to a paraelectric phase was determined with temperature when a dielectric constant is the highest. Moreover, the stability with the passage of time in room temperature neglect was measured from the specific inductive capacity and dielectric loss to 1kHz, and resistivity was measured by the 2 terminal I-V method from the amperometry value and voltage value 30 minutes after voltage impression.
[0021] as shown in the aforementioned table 1, if the measurement result of the first sample (KNN-CuO) of 1 hour after polarization and a basis sample (KNN) is compared, according to the first sample of this invention article, relative density is going up, and also the electromechanical coupling coefficient (kp) as a piezo-electric property, a piezoelectric constant (g31, g33), and the mechanical quality factor (Qm) as elasticity are markedly alike, and the high value is shown Moreover, there is also little dielectric loss (tandelta) as dielectric characteristics, the dielectric constant (% / -50-100 degrees C) change to a temperature change is small, and it turns out that resistivity (ohm-cm) shows the high value.
[0022] Moreover, as shown in Table 2, that the same measurement result is improving turns out that the measurement result of the first sample (KNN-CuO) of the above on the 28th after polarization and a

basis sample (KNN) was shown in Table 1. Moreover, it was checked that CuO acts on each property and the measurement result which improved acts also on stability with the passage of time further since a big change is not seen even if 28 days after polarization pass.

[0023] Drawing 1 is the graph which showed the relation between the sintering temperature in the first sample (KNN-CuO) of the above, and a basis sample (KNN), and density. According to this, in all sintering temperature, densification of the first sample is carried out rather than the charge (KNN) of a base material, and it is understood that sintering temperature order of 1050 degrees C -, and 1125-degree-C order is the highest-density. It is to turn and for density to rise precisely by what, as for this, the liquid phase produces it before and after 1050 degrees C - 1125 degrees C since CuO has the melting point in 1025 degrees C, and between the solid phase particles of a crystal is filled with liquid flow for (or it replaces). Acting from this as a sintering acid to which CuO carries out densification of the sample was checked.

[0024] Drawing 2 is the graph which showed change of the dielectric constant under constant temperature (room temperature of 25 degrees C) for every lapsed days. It turns out to a value increasing the dielectric constant of a basis sample (KNN) gradually according to this graph that the dielectric constant of the first sample (KNN-CuO) is mostly stable over 270 days. Furthermore, as shown in drawing 3 , the first sample of the above is in a stabilization inclination over 270 days to the dielectric loss of the aforementioned machine sample increasing in connection with lapsed days. And the dielectric constant change to a temperature change is also understood that the first sample is lower again so that it may illustrate to drawing 4 .

[0025] This is for acting so that pinning of the domain under crystal may be carried out and it may fix, when CuO deposits in that CuO carries out substitution dissolution during the crystal of a sample and/, or a grain boundary. If a domain generally moves, dielectric loss is large and the bird clapper is known. Therefore, improvement in a machine quality factor (Qm) can be aimed at at the same time it stabilizes dielectric loss by fixing a domain. Moreover, in order to reduce a dielectric constant, without changing a piezoelectric constant d, a piezoelectric constant g improves greatly. It was checked that a degree of sintering is obtained from this with an ordinary-pressure sintering process with an existing material with the well high stability with the passage of time over lapsed days.

[0026] Moreover, although not illustrated, it passes through it while the piezoelectric constant g of this addition of CuO will improve, if it adds by 0.001-mol % - 5.0-mol% of within the limits, and its Tokiyasu quality improves, and it acts as a sintering acid especially by 0.1-mol % - 2.0-mol% of within the limits. However, in being fewer than the aforementioned addition, it does not act as a sintering acid, but the fall of a property is seen when many. As for the addition of this copper oxide, about 1 mol % is considered to be a proper quantity by the above.

[0027] Next, the sample (the second sample) which added Li and Ta in the basis sample which consists of empirical-formula K1-xNaxNbO(s)3 (0<=x<=0.8) is explained.

[0028] (Example 2) LiCO3 of 99% or more of purity, K2CO3, NaHCO3 and Nb 2O5, and Ta2O5 are respectively used for the sample (the second sample : KNN-LT) used for this example 2. Each of these powder was blended so that it might become the empirical formula of O(Nb (Li0.1K0.45Na0.45) 0.8, Ta0.2) 3, and the weighing capacity of a total of 50g was obtained. And it manufactures like the manufacturing process shown in the aforementioned example 1. Sintering was performed at 1125 degrees C. In addition, since this manufacturing process is mentioned already in the example 1, it omits about the explanation.

[0029] And the measurement result in the stage which passed after polarization of the second sample (KNN-LT) of the above for 1 hour is shown in Table 3, and the measurement result in the stage which passed after polarization on the 28th is shown in Table 4. moreover, the measurement result of the basis sample (KNN) simultaneously sintered at 1100 degrees C which has not added Li and Ta -- respectively -- being shown . It was decided with temperature when a dielectric constant is the highest about Curie temperature using the resonance antiresonating method like the aforementioned example 1 that it would be measurement and evaluation of this sample.

[0030]

[Table 3]

ＫＮＮ－ＬＴの測定結果（分極後１時間）

	本発明品（第二試料）	比較品（基試料）	
試料名	ＫＮＮ－ＬＴ	ＫＮＮ	
組成式	$\{(K_{0.5}Na_{0.5})_{0.9}Li_{0.1}\}(Na_{0.8}Ta_{0.1})O_3$	$K_{0.5}Na_{0.5}NbO_3$	
測定項目			
相対密度（％）	９９．０	９６．２	
圧電特性			
電気機械結合係数（ｋｐ）	０．３０７	０．３３４	
圧電定数（ｄ３１ pm/V）	３６．３	３７．６	
圧電定数（ｄ３３ pm/V）	１０４	１１５	
圧電定数（ｇ３１ 10^{-3}Vm/N）	６．５７	９．９０	
圧電定数（ｇ３３ 10^{-3}Vm/N）	１１．９	３０．３	
弾性特性			
機械的品質係数（Ｑm）	２７３．４	１００．６	★
誘電特性			
誘電率（Ｅ３３ｔ）	６２４	４２９	
誘電損失（ｔａｎδ）	０．００７１	０．０３５６	★
相転移温度			
キュリー温度（℃）	３８０	４１５	
相転移温度（Ortho→Tetra）	なし	２１０	★
温度変化率			
誘電率（％／-50～100℃）	１０	９３	★
抵抗率（Ω・cm）	３．１５E＋１０	７．６７E＋１０	

（注）★：Ｌｉ、Ｔａにより向上している特性

[0031]
[Table 4]

KNN-LTの測定結果 (分極後28日)

	本発明品 (第二試料)	比較品 (基試料)	
試料名	KNN-LT	KNN	
組成式	{(K0.5Na0.5)0.1Li0.1}(Na0.8Ta0.1)O3	K0.5Na0.5NbO3	
測定項目			
相対密度 (%)	99.0	96.2	
圧電特性			
電気機械結合係数 (kp)	0.290	0.329	
圧電定数 (d31 pm/V)	33.4	38.6	
圧電定数 (d33 pm/V)	104	115	
圧電定数 (g31 10^-3 Vm/N)	6.23	9.30	
圧電定数 (g33 10^-3 Vm/N)	11.6	30.3	
弾性特性			
機械的品質係数 (Qm)	360.1	85.6	★
誘電特性			
誘電率 (E33t)	606	470	
誘電損失 (tanδ)	0.0070	0.0890	★
相転移温度			
キュリー温度 (℃)	380	415	
相転移温度 (Ortho→Tetra)	なし	210	★
温度変化率			
誘電率 (%/-50~100℃)	10	93	★
抵抗率 (Ω・cm)	3.15E+10	7.67E+10	

(注) ★: Li、Taにより向上している特性

[0032] As shown in the aforementioned table 3, if the measurement result of the second sample (KNN-LT) of 1 hour after polarization and a basis sample (KNN) is compared, improvement will be found by the mechanical quality factor (Qm), and also dielectric loss (tandelta) is low loss small, and it turns out that the temperature stability that the rate of a temperature change of a dielectric constant becomes small (% / -50-100 degrees C) is good. Moreover, as shown in Table 4, the measurement result and great difference which were after [polarization] shown in the aforementioned table 3 also in the measurement result after progress on the 28th are not seen. Therefore, Li and Ta acting on temperature stability, and acting also on stability with the passage of time was checked.

[0033] Drawing 5 is the graph which showed the relation between the density in the second sample (KNN-LT) of the above, and a basis sample (KNN), and sintering temperature. According to this, it turns out that the second sample of the above is carrying out densification. This is for the state (liquid phase sintering) where the component and phase of Li oxide which were added liquid-phase-ize with the rise of sintering temperature to sintering of material usually being performed by solid phase sintering, and the component and phase of a part for this liquid phase Chemicals and other material which solidified without liquid-phase-izing live together and sinter to arise. Densification of material can be attained by this.

[0034] Drawing 6 is the graph which showed the dielectric constant under constant temperature (room temperature of 25 degrees C), and the relation of lapsed days. Since the value had the value stabilized mostly even if days passed on the 245th although the direction of the second sample of the above was a high dielectric constant so that it might illustrate, it was checked that stability with the passage of time is good. Moreover, drawing 7 is the graph which showed the dielectric loss under constant temperature (room temperature of 25 degrees C), and the relation of lapsed days. According to this graph, it turns out that the value which the second sample (KNN-LT) was not concerned with the progress whose days are 245 days, but was stabilized is maintained. This is for playing the role to which Ta carries out pinning of the domain under crystal. As mentioned already, the value which movement of a domain made dielectric loss low by fixing a domain since it originates in the increase in dielectric loss, and was stabilized is acquired.

[0035] Drawing 8 is the graph which showed the relation between the dielectric constant in the second sample (KNN-LT) of the above, and a basis sample (KNN), and temperature. In the second sample of the above, the middle transition phase (before or after 210 degrees C) was lost, and it was checked that the dielectric constant stabilized mostly is obtained so that it might illustrate. this -- Li -- more than 5.0 mol % -- when it adds, it is for a crystal phase to transfer to a tetragonal phase from a prismatic crystal, and it is considered what a middle transition phase is lost and the temperature characteristic stabilizes by this As for the material which has the same high dielectric constant temperature stability, the amount of Ta was obtained by composition not more than 40 mol %.

[0036] Moreover, although not illustrated, Above Li acts as a sintering acid between addition % of 0.1 mols -, and 20-mol %, and although densification of the material is carried out, it is checked more than at 20 mol % that $LiNbO_3$ arises and a piezo-electric property falls from a mixed phase and a bird clapper.

[0037] (Example 3) Li_2CO_3 of 99% or more of purity, $NaHCO_3$ and Nb_2O_5, and Ta_2O_5 are respectively used for the sample used for this example 3. each of these powder was blended so that it might become the empirical formula of Lix $(K_{0.5}Na_{0.5})$ 1-x $(Nb_{1-y}Ta_y)O_3$ (30 however, x= 0, 0.02, 0.04, 0.06, 0.08, 0.10, 0.15, 0.20; y= 0, 0.10, 0.20, 0. 0.40), and sum totals [of 50g of each] weighing capacity was obtained And it manufactures like the process shown in the aforementioned example 1. In addition, since the example 1 has described this manufacturing process, it omits about the explanation. As an example of comparison, the charge of a base material (KNN;x=0, y= 0) which has not added Li and Ta was produced similarly.

[0038] The sintering temperature of each sample chose the temperature which turns into the maximum density among 1025 degrees C - 1250 degrees C. Each sample has turned into 98% or more of relative density precisely altogether except for 96.2% of the charge (KNN) of a base material.

[0039] The measurement result of electromechanical-coupling-coefficient (kp) piezo-electricity d31 in the stage which passed after the above and polarization of each sample for 1 hour constant, and piezo-electric g31 constant is shown in drawing 9 (a), (b), and (c). Moreover, the measurement result of the basis sample (KNN) which has not added Li and Ta simultaneously was also shown to Li= zero-mol % and Ta = zero-mol% in drawing 9 .

[0040] About Curie temperature, it was decided with temperature when a dielectric constant is the highest using the resonance antiresonating method like the aforementioned example 1 that they would be measurement of this sample and evaluation.

[0041] About the electromechanical coupling coefficient (kp) shown in drawing 9 (a), it becomes a value higher than a basic material (KNN) at Li addition =0 - six-mol % in % of a Ta addition =10 - 40-mol composition field. The greatest value was acquired at Li addition = four-mol addition [% and Ta] = 20-mol %. A piezoelectric-transformer element or an ultrasonic motor element with an electric conversion efficiency higher than the case where a basic material (KNN) is used, and a ultrasonic vibrator can be made from using the material of this composition.

[0042] Piezo-electric d31 constant shown in drawing 9 (b) serves as a value higher than the charge (KNN) of a base material at Li addition =0 - six-mol % in % of a Ta addition =10 - 40-mol composition field. As for the greatest value, d31=95 pm/V was obtained by the Ta addition =20 mol Li addition =4

mol%. Since piezo-electric d constant is proportional to the output voltage of piezo-electricity type sensors, such as acceleration at the time of using a charge (or current) detection type circuit, a load, a shock, and a knock sensor, a sensor with a bigger charge sensor output than the charge (KNN) of a base material can be made from using the material of % of a Ta addition = 10-40-mol composition field at this Li addition = 0-6-mol %.

[0043] Piezo-electric g31 constant shown in drawing 9 (c) serves as a value higher than a basic material (KNN) by Li addition = zero-mol % with Ta addition = zero-mol% of composition at Ta addition = 10 or 20-mol% of composition and, and Li= 2 or 4-mol %. As for the greatest value, g31=14.5x10-3 Vm/N was obtained at Li addition = two-mol addition [% and Ta] = zero-mol %. Since piezo-electric g constant is proportional to the output voltage of piezo-electricity type sensors, such as acceleration at the time of using a voltage detection type circuit, a load, a shock, and a knock sensor, sensor parts with a piezo-electric bigger sensor output than the charge (KNN) of a base material can be made from using the material of this composition field.

[0044] About the Curie temperature shown in drawing 10 (a), Curie temperature falls gradually with the increase in Ta addition in composition of each Li addition regularity. Moreover, in composition of Ta addition regularity, Curie temperature turns into high temperature gradually with the increase in Li addition. It is checked that the temperature stability of a piezoelectric constant deteriorates [Curie temperature] in a composition field 250 degrees C or less.

[0045] The dielectric constant shown in drawing 10 (b) is Ta=. In composition of 0mol% regularity It is maximum = at Li= six-mol %. In composition of 864Ta=10mol% regularity It sets to composition of maximum =1014Ta=20mol% regularity at Li= six-mol %. In composition of maximum =1204Ta=30mol% regularity, it became [Li= four mol %] maximum =1837 at Li= zero-mol % in composition of maximum =1466Ta=40mol% regularity by Li= two-mol %.

[0046] The dielectric loss shown in drawing 10 (c) serves as a value of dielectric loss lower than a basic material (KNN) at Li addition =0 - 20-mol% with Ta addition =10 - 40-mol% of composition and, and Li=2 or 4-mol addition [% and Ta] =zero-mol% of composition. Since the square root of dielectric loss is proportional to the noise of the output voltage of piezo-electricity type sensors, such as acceleration, a load, a shock, and a knock sensor, mostly, rather than the charge (KNN) of a base material, a noise is small and can make the high high sensitivity voltage sensor of a S/N ratio from using the material of this composition field.

[0047] From the above thing to Lix 1-x (Nb1-yTay)O3 (K0.5Na0.5) The material of (however x= 0, 0.02, 0.04, 0.06, 0.08, 0.10, 0.15, 0.20;y=0, 0.10, 0.20, 0.30, and 0.40) Above 250 degrees C, Curie temperature is excellent at temperature stability, piezo-electric d31 constant or piezo-electric g31 constant is larger than the charge (KNN) of a base material, and dielectric loss is small, and the charge of piezo-electricity type sensor material with few noises can be manufactured.

[0048] Piezo-electricity type sensors, such as acceleration which is excellent in temperature stability and has the charge detector type or voltage detector type circuit where sensor output voltage is big by using the material of this composition field and which used piezoelectric material for the detecting element, a load, a shock, and a knock sensor, can be manufactured.

[0049] Alterations various in the range which is not limited to the above-mentioned example at all, and does not deviate from the meaning of this invention are possible for this invention. For example, although the material which consists of empirical formulas (KxNax) NbO3 as an alkali-metal system material in the above-mentioned example was used, it is also possible to change other material and the additive of those. It becomes possible to manufacture a high material of a degree of sintering and stability with the passage of time, and temperature stability by this.

[0050]

[Effect of the Invention] According to the niobic-acid system piezoelectric material concerning this invention, to the solid solution expressed with an empirical formula (ANbO3) (A : alkali metal) Cu, Add or one sort or two sorts or more of matter chosen from Li and Ta is made to dissolve. like invention according to claim 2 as one example To the solid solution expressed with empirical-formula Kl-xNaxNbO3 (however, x=0-0.8), like a publication at a claim 4 If it adds or the compound containing Cu

element is made to dissolve so that Cu may become 0.001-5-mol % in the amount of elements, the densification of the material can be carried out by sintering-acid operation of the compound containing Cu element. Furthermore, since the deposit to the substitution dissolution operation of a compound and/, or the grain boundary containing Cu element protects a dielectric loss fall, stability with the passage of time is good, and the outstanding piezo-electric property is acquired. And since lead system material is not contained, safety becomes possible [manufacturing the material which has high performance highly].

[0051] Moreover, by adding Li and Ta like invention according to claim 3 concerning this invention If the alkali-metal content niobic-acid ghost system piezoelectric-material constituent expressed with an empirical formula $Li_x (K_{1-y}Na_y)_{1-x} (Nb_{1-z}Ta_z)O_3$ (however, x= 0.001 to 0.2, y= 0 to 0.8, z=0-0.4) is produced Since Li acts on the densification of material as a sintering acid, Ta acts on the domain in the solid solution and reduction of dielectric loss and improvement in the rate of dielectric loss can be aimed at, an alkali-metal content niobic-acid ghost system piezoelectric-material constituent according to claim 3 serves as a material excellent in stability with the passage of time and temperature stability. And from not containing lead system material, these can also be used for a large use.

[0052]

[Translation done.]

* NOTICES *

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is the graph which showed the relation between the sintering temperature in this example 1, and density.
[Drawing 2] It is the graph which showed the relation between the dielectric constant in an example 1, and lapsed days.
[Drawing 3] It is the graph which showed the relation of the dielectric loss and lapsed days in an example 1.
[Drawing 4] It is the graph which showed the relation between the dielectric constant in an example 1, and temperature.
[Drawing 5] It is the graph which showed the relation between the density in an example 2, and sintering temperature.
[Drawing 6] It is the graph which showed the relation between the dielectric constant in an example 2, and lapsed days.
[Drawing 7] It is the graph which showed the relation between the dielectric loss in an example 2, and lapsed days.
[Drawing 8] It is the graph which showed the relation between the dielectric constant in an example 2, and temperature.
[Drawing 9] The empirical formula [in / an example 3 / in (a), (b), and (c)] $Li_x (K_{0.5}Na_{0.5}) _{1-x} (Nb_{1-y}Ta_y)O_3$ It is the graph which showed change of the piezo-electric property by the amount of Li of (however x= 0, 0.02, 0.04, 0.06, 0.08, 0.10, 0.15, 0.20;y=0, 0.10, 0.20, 0.30, and 0.40), and Ta.
[Drawing 10] The empirical formula [in / an example 3 / in (a), (b), and (c)] $Li_x (K_{0.5}Na_{0.5}) _{1-x} (Nb_{1-y}Ta_y)O_3$ It is the graph which showed change of the Curie temperature by the amount of Li of (however x= 0, 0.02, 0.04, 0.06, 0.08, 0.10, 0.15, 0.20;y=0, 0.10, 0.20, 0.30, and 0.40), and Ta, a dielectric constant, and dielectric loss.
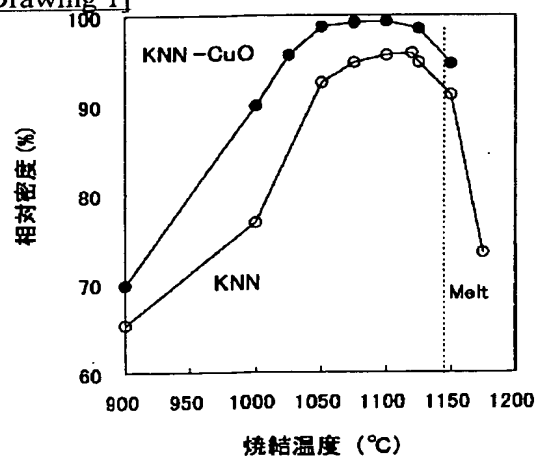

[Translation done.]

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2.**** shows the word which can not be translated.
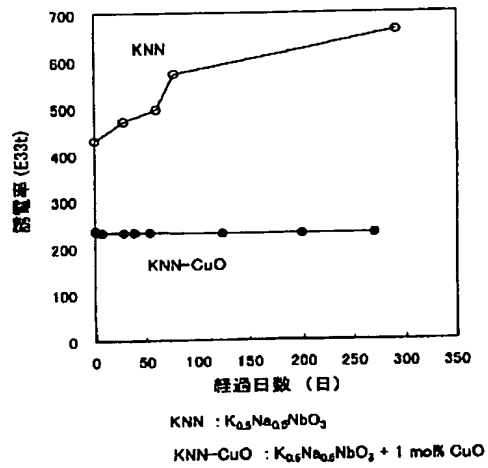3.In the drawings, any words are not translated.

DRAWINGS

[Drawing 1]

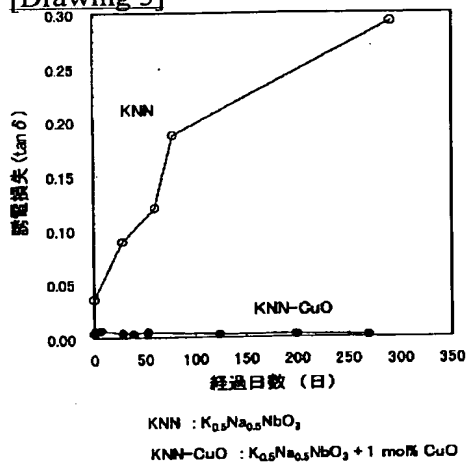KNN : $K_{0.5}Na_{0.5}NbO_3$

KNN –CuO: $K_{0.5}Na_{0.5}NbO_3$

[Drawing 2]

KNN : $K_{0.5}Na_{0.5}NbO_3$

KNN-CuO : $K_{0.5}Na_{0.5}NbO_3$ + 1 mol% CuO

[Drawing 3]

KNN : $K_{0.5}Na_{0.5}NbO_3$

KNN-CuO : $K_{0.5}Na_{0.5}NbO_3$ + 1 mol% CuO

[Drawing 4]

KNN : $(K_{0.5}Na_{0.5})NbO_3$

KNN-CuO : $(K_{0.5}Na_{0.5})NbO_3+1mol\% CuO$

[Drawing 5]

KNN : $K_{0.5}Na_{0.5}NbO_3$

KNN -LT: $[(K_{0.5}Na_{0.5})_{0.9}Li_{0.1}](Nb_{0.8}Ta_{0.2})O_3$

[Drawing 6]

KNN : $K_{0.5}Na_{0.5}NbO_3$

KNN-LT : $[(K_{0.5}Na_{0.5})_{0.8}(Nb_{0.8}Ta_{0.2})O_3$

[Drawing 7]

KNN : $K_{0.5}Na_{0.5}NbO_3$

KNN-LT : $[(K_{0.5}Na_{0.5})_{0.8}(Nb_{0.8}Ta_{0.2})O_3$

[Drawing 8]

縦軸: 誘電率 (E33t)

横軸: 温度 (℃)

凡例:
— KNN
····· KNN-LT

KNN : $(K_{0.5}Na_{0.5})NbO_3$

KNN-LT : $K(K_{0.5}Na_{0.5})_{0.9}Li_{0.1})(Nb_{0.8}Ta_{0.2})O_3$
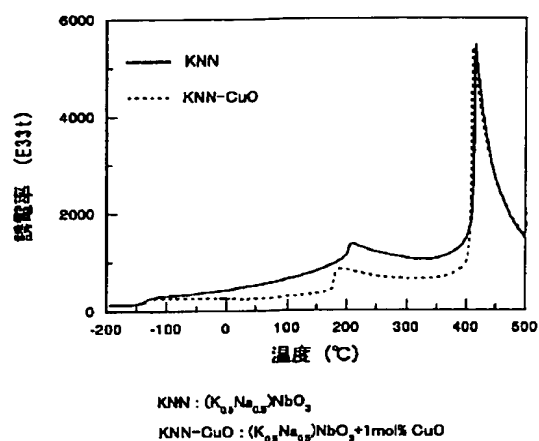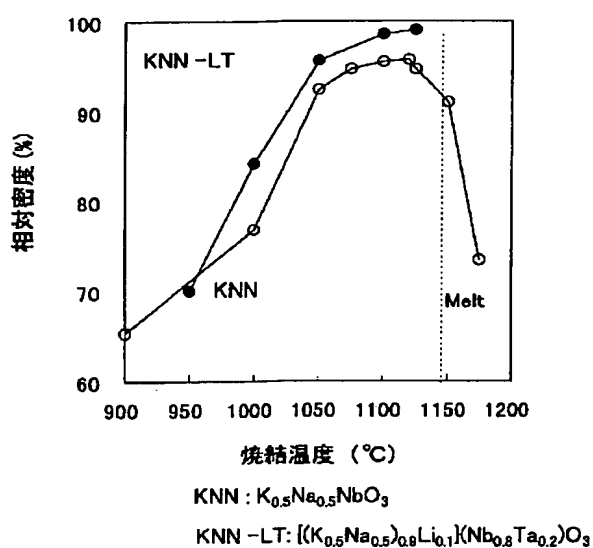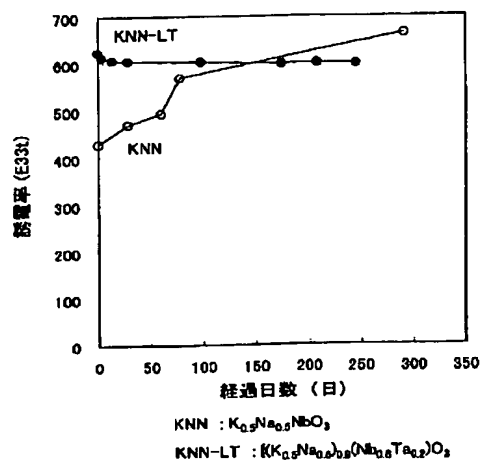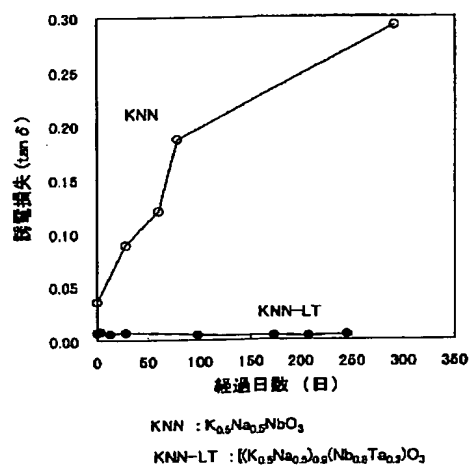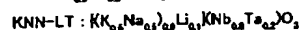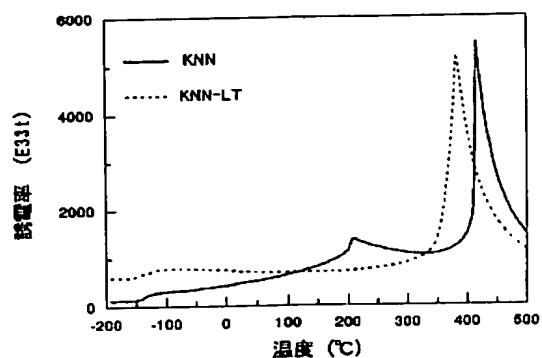
[Drawing 9]

(a) 電気機械結合係数 (Kp)

Li (mol%) \ Ta (mol%)	0	10	20	30	40
20	0.092	0.170	0.187	0.150	0.160
15	0.087	0.203	0.230	0.209	0.204
10	0.151	0.292	0.307	0.292	0.283
8	0.196	0.340	0.335	0.313	0.287
6	0.332	0.415	0.383	0.406	0.336
4	0.371	0.456	0.501	0.431	0.382
2	0.469	0.395	0.341	0.380	0.330
0	0.334	0.453	0.465	0.332	0.294

(b) 圧電定数 (d31 pm/V)

Li (mol%) \ Ta (mol%)	0	10	20	30	40
20	9.7	20.2	21.5	16.4	17.3
15	10.1	23.2	25.1	23.7	22.0
10	20.4	39.6	36.3	32.6	33.2
8	27.5	50.8	46.1	41.2	36.6
6	57.7	71.0	60.1	58.3	46.3
4	39.8	69.5	95.0	73.1	63.5
2	48.9	51.4	54.3	79.3	70.1
0	37.6	49.5	60.5	82.9	66.0

(c) 圧電定数 (g31 10^{-3} Vm/N)

Li (mol%) \ Ta (mol%)	0	10	20	30	40
20	2.8	4.2	4.5	3.7	3.6
15	2.2	4.8	5.4	4.6	4.6
10	3.5	6.7	6.8	6.6	6.3
8	4.7	6.8	6.8	6.1	6.4
6	7.5	7.9	7.1	7.7	6.0
4	11.0	10.3	9.0	7.5	6.2
2	14.5	9.3	6.8	6.1	4.7
0	9.9	12.1	10.5	6.0	4.1

[Drawing 10]

(a)

キュリー温度 (°C)

Li (mol%) \ Ta (mol%)	0	10	20	30	40
20	505	459	390	347	295
15	502	450	385	337	280
10	499	450	380	330	262
8	485	420	363	310	250
6	474	405	345	295	235
4	460	393	337	279	220
2	435	375	308	250	192
0	415	350	285	233	168

(b)

誘電率 (E33t)

Li (mol%) \ Ta (mol%)	0	10	20	30	40
20	399	540	539	504	542
15	530	544	521	580	646
10	657	672	624	666	699
8	657	847	762	761	625
6	864	1014	959	855	868
4	409	763	1204	1106	1165
2	364	621	903	1466	1688
0	429	462	652	1187	1837

(c)

誘電損失 (tan δ)

Li (mol%) \ Ta (mol%)	0	10	20	30	40
20	0.091	0.015	0.011	0.014	0.008
15	0.045	0.022	0.007	0.007	0.008
10	0.088	0.039	0.007	0.007	0.008
8	0.037	0.010	0.010	0.008	0.011
6	0.050	0.008	0.006	0.008	0.011
4	0.014	0.014	0.008	0.006	0.014
2	0.003	0.023	0.018	0.016	0.018
0	0.038	0.005	0.010	0.012	0.009

[Translation done.]